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(54) Title: PEROXYGEN LAUNDRY BLEACH (57) Abstract The invention provides a process to coat dry particles comprising sodium carbonate perhydrate to provide a stable dry particulate solid which releases hydrogen peroxide when contacted with an aqueous solution. The coated particles are readily soluble in water and/or stable when formulated into a solid detergent.		

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PEROXYGEN LAUNDRY BLEACH

The present invention is a solid composition which releases hydrogen peroxide in the presence of water and is stable when incorporated into solid household and laundry detergents.

It is well known that peroxygenated compounds can be used as bleaching compounds in detergent powder mixtures. In the usual household detergents, sodium perborate tetrahydrate is generally used as a bleaching compound even though it is phytotoxic, as it is relatively stable to decomposition in a powdered detergent medium. However, sodium perborate tetrahydrate has the disadvantage of dissolving too slowly, particularly in cold water. Sodium perborate monohydrate, on the other hand, dissolves rapidly, however, the particles are very fragile and generally break down to a dust. Both forms are environmentally undesirable because they add 1 mole of boron compound to the environment for each mole of active oxygen.

To rectify this disadvantage, it has been suggested that powdered detergents be used in a mixture with other peroxygen compounds, notably alkali metal percarbonates, perphosphates and peroxymonosulfates, which have suitable dissolution rates. These peroxygen compounds, particularly percarbonates, decompose too quickly in the powdered state, especially if they are stored in a humid atmosphere. Furthermore, the moisture and other constituents in the cleaning compounds accelerate this decomposition.

It has been suggested that particles of peroxygen compounds be coated by various compounds, such as trona (U.S. Patent No. 4,105,827); sodium silicate (U.S. Patent No. 3,951,838); sodium perborate plus sodium silicate (U.S. Patent No. 4,194,025); boric acid (U.S. Patent No. 4,321,301); wax (U.S. Patent No. 4,421,669); a polymer latex (U.S. Patent No. 4,759,956); sodium silicate plus a chelate (U.S.

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Patent No. 4,117,087); and wax plus a fatty acid (U.S. Patent No. 4,126,717). Many of these treatments show some improvement in short term storage stability in a humid environment.

5 In general, these processes are based on either
1) physically coating the sodium carbonate peroxide
with a compound, such as, trona, boric acid and the
like to prevent the peroxygen compound (for example,
sodium carbonate perhydrate) from physically contact-
10 ing the other compounds in the detergent composition
as a spacer, or 2) coating the peroxygen compound
with a vapor barrier such as a wax or a polymer.
Neither of these processes has been successful as a
mere physical coating permits water vapor to pene-
15 trate the particle to initiate decomposition, while
coating with a vapor-impervious barrier retards the
rate of solution of the particle so much that the
compound is unusable.

20 The present invention overcomes the difficulties
of the prior art by providing a process for preparing
a storage-stable compound comprising:

a) suspending substantially dry particles com-
prising a sodium carbonate perhydrate containing
between 0.1% and 3% by weight diphosphonic acid or
25 salt and between 1 and 5 moles of anhydrous sodium
carbonate for each mole of available water contained
therein sufficiently to substantially eliminate
solid-solid contact between particles,

b) contacting said dry particles with a plurality
30 of fine drops of an aqueous solution consisting
essentially of a mixture of 1 to 99 parts by weight
sodium silicate and from 99 to 1 parts by weight
sodium metaborate,

c) concomitantly evaporating substantially all
35 this water at a sufficient rate to avoid moistening
or hydrating the dry particles, thereby providing

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from 2% to 10% by weight coating said dry particles,
and

d) collecting the coated dry particles as a free-flowing peroxygen compound stable when incorporated
5 into a solid detergent formulation. The coated particles may be recycled to step a) and thereby be provided with two or more coatings.

The scope of the present invention is intended to include the product made by said process.

10 Any composition containing dry particles comprising sodium carbonate perhydrate, with from 1 to 5 moles excess sodium carbonate (anhydrous) and 0.1% to 3% diphosphonic acid may be employed.

One skilled in the art can easily prepare a preferred nonstoichiometric sodium carbonate perhydrate
15 composition, "Soda Ash Peroxygen Carrier", (SAPC) according to the process described in U.S. Patent No. 4,966,762. The process comprises applying a solution of a diphosphonic acid or salt, preferably 1-
20 hydroxyethylidene-1,1-diphosphonic acid in aqueous hydrogen peroxide to particles of anhydrous sodium carbonate, concomitantly removing water vapor from the surface of the reaction mixture, and maintaining the temperature of the reaction mixture between about
25 35°C and 80°C, said diphosphonic acid or salt being present in an amount to provide 0.1% to 3% diphosphonic acid or salt in the composition thereby providing as product a soda ash peroxygen carrier containing between 1 and 5 moles of sodium carbonate for
30 each mole of available water in the composition, said available water consisting essentially of water chemically available as hydrogen peroxide, water of crystallization and free water.

Diphosphonic acid appears to slow the rate of
35 hydration of anhydrous sodium carbonate so that water preferentially evaporated. However, after the product is dried, the anhydrous sodium carbonate appears

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to be able to form a hydrate with any water formed by the decomposition of the peroxygen. Thus pure soda ash peroxygen carrier (SAPC) is less subject to accelerated decomposition than sodium carbonate perhydrate.

5 Apparently, one problem with the prior art coating processes is that the sodium carbonate perhydrate decomposition process produces 1.5 moles of water for each mole of sodium carbonate perhydrate, and the
10 coating, if impervious to vapor, prevents the water from evaporating. Consequently, the retained water accelerates the decomposition of the sodium carbonate perhydrate. On the other hand, when the coating is
15 not impervious to water vapor, the moisture in the detergent formulation is able to contact the sodium carbonate perhydrate and initiate decomposition.

The present invention can be carried out in a fluid bed by suspending the dry particles by the fluidizing gas and applying the coating by a spray.
20 For the purpose of this invention "suspending ... to eliminate solid-solid contact" would include permitting particles to be separately lifted by a stream of air or to fall separately as in a tower. Alternatively, the invention can be carried out in a tower and
25 applying the coating in a countercurrent, cocurrent, or radial spray. Other alternative processes will be apparent to one skilled in the art, such as a spray dryer with both liquid and solids injection, or the like.

30 It is critical for the present invention that the drops of aqueous solution be much smaller in diameter than the solid particles to avoid agglomerating the particles caused by wetting the surface of the dry particles, or of hydrating either the sodium carbonate perhydrate (SPC) or any sodium carbonate in the
35 dry particles thereby forming the hydrate of SPC,

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2Na₂CO₃·3H₂O·2H₂O₂, a sodium carbonate hydrate or other hydrate. It is well known that once formed, sodium carbonate monohydrate is very difficult to dehydrate without concomitantly decomposing an active oxygen compound associated with it.

The best mode of practicing the invention will be clear to one skilled in the art from the following nonlimiting examples. Unless specified otherwise, percentages are reported as percent by weight.

10 STABILITY TESTS

The Quick Test is a method for determining the relative stability of similar samples (decomposition) in only eight hours. Sufficient sample is added to a closed container connected to a manometer to provide a constant volume to sample weight ratio. The temperature is maintained at 50°C and the oxygen evolved (the increase in pressure is measured hourly by the and the slope of the line is reported as cm/Hg). The test can be employed for samples formulated in a detergent base or for unformulated samples of a per-oxygen compound ("neat stability").

The 80/80 Open Box Test simulates the storage of an open box of a detergent formulation. Unless otherwise specified sufficient peroxygen compound to be evaluated is blended in a commercial detergent formulation to provide 0.7% active oxygen by weight. The box containing 0.45 kilograms of formulation is stored with an open lid at 26.7°C (80°F) and 80% relative humidity for six weeks. At two week intervals samples are selected by riffing the contents of the box. Active oxygen is determined in triplicate.

30 COATING PROCESS

The apparatus used for coating the dry particles was the Strea-1 Laboratory Fluid-Bed Coater, manufactured by Aeromatic, a division of Niro Industries.

The unit consists of a coating feed container, a tubing pump to dispense the coating solution and the

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fluid bed coater. The fluid bed coater consists of a clear outer shell for easy viewing, a grid plate to introduce the fluidizing air, and a center draft tube containing an air atomizing spray nozzle. The product introduced into the container is fluidized by a stream of preheated air from below the grid plate. The particles to be coated are recycled through the draft tube until the desired amount of coating is applied.

10 COATING PROCEDURE

1. Adjust the space between the grid plate and the bottom of the center tube to the specified setting.

2. Adjust the nozzle atomizing air to the desired setting by adjusting the nozzle spray cap.

3. Preheat the fluid bed apparatus to coating temperature.

4. Load the required amount of peroxygen compound into the bed coater.

20 5. Heat the contents using preheated air which is used to fluidize the contents at mild fluidizing velocity.

6. After the bed temperature of 38°-71°C (100°-160°F), preferably 48°-60°C (120°-140°F) is attained, increase the air atomizing rate and fluid bed velocity and start the coating application preferably at the predetermined rate.

7. During the coating application, maintain the bed temperature by adjusting the inlet air rate and temperature. Also maintain coating application rate.

8. After the required amount of coating is applied, reverse the coating pump to empty the lines of coating material back to the the feed container, deactivate the air preheater, stop the fluid air to the fluid bed and empty the contents of the container.

9. Weigh the coated material.

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The coating process employed a variety of materials: sodium silicate, sodium metaborate, sodium borosilicate, sodium bicarbonate, sodium carbonate, sodium polyacrylate, polyethylene glycol and polypropylene glycol.

It is essential to avoid substantial agglomeration of particles. Agglomeration is easily measured by a decrease in bulk density. For example uncoated SAPC having a bulk density of $1,025 \text{ kg/m}^3$ (64 lb/cu.ft.) should have a bulk density after coating of at least 800 kg/m^3 (50 lb/cu.ft.), preferably at least 880 kg/m^3 (55 lb/cu.ft.).

The particles are coated with 2-10% of their weight of coating compound. The single coating material may be applied or a combination either as a mixture or as multiple coats. The effect of the coating is determined by how well the coated particles maintain active oxygen (hydrogen peroxide content) in the Quick Test and Open Box Test.

Solutions of the coating compound can vary in concentration over a large range. Preferably the solutions should contain about 15% to 25% solids. Higher concentrations than 25% can be used but usually must be preheated to prevent crystallization and to permit atomization into fine droplets. More dilute solutions require a greater heat input to evaporate the water sufficiently to prevent wetting the particles being coated. With care solutions can range from about 12% solids to about 35% solids.

Typical 25% solids solution preparation is illustrated as follows:

Sodium metaborate: Add 261.8 g sodium metaborate tetrahydrate to 238.2 g water.

Sodium silicate: Add 334.4 g of a 37.4% solution of sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ weight ratio = 3.22) to 165.8 g water.

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Sodium borosilicate: A blend of above solutions (ratio 1:99 to 99:1).

The best mode of practicing the invention is exemplified employing the preferred SAPC because it will easily detect insufficient evaporation of water in step c) by the conversion of anhydrous sodium carbonate to a hydrate.

EXAMPLE 1

Soda Ash Peroxygen Carrier (SAPC) initially containing about 9.0% active oxygen was prepared using two commercial grades of sodium carbonate, FMC Corporation's Grade 100 soda ash and Grade 90 soda ash. Samples were coated and the stability was determined by the Quick Test as cm/hr. The experimental details and results are reported as Table I. The Grade 90 soda ash is more absorptive than the Grade 100.

From the Table it is clear that the type of sodium carbonate has no effect on the stability of the SAPC produced, either before or after coating. Generally, coating the SAPC decreases the decomposition rate.

EXAMPLE 2

Coated and uncoated SAPC were evaluated by the Quick Test alone (neat stability) and formulated with a commercial detergent (P&G's nonphosphate Tide). Sufficient SAPC was employed to provide 0.7% active oxygen (AO) in the formulation. The results are presented as Table II.

In comparing the decomposition rate it is important to recognize the difference in % active oxygen (AO). All "Detergent Formulations" samples initially contained 0.7% AO while the neat stability samples contained 10 to 13 times as much (from 7.0 - 9.4% AO).

The Table shows particles coated according to the present invention are far more stable (less decom-

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position) in detergent formulations than uncoated particles and comparable to the sodium perborate monohydrate of Tide with Bleach.

EXAMPLE 3

5 Samples of SAPC coated with sodium silicate, sodium metaborate, sodium borosilicate were evaluated in the Open Box Test. Results are presented as Table III. Commercial Tide with Bleach containing 0.7% AO as sodium perborate monohydrate was employed as a
10 control.

From Table III it is clear that the coated samples are generally more stable than a commercial formulation containing "stable" sodium perborate monohydrate.

15

EXAMPLE 4

Under identical temperature and stirring conditions a SAPC coated with 2% borosilicate was 95% dissolved after 1 minute at 15°C while a sample of sodium perborate tetrahydrate was only 30% dissolved.
20 Even a SAPC coated with 10% borosilicate was 88% dissolved in the same time.

EXAMPLE 5

25 Samples of soda ash peroxygen carrier made by the process of U.S. Patent No. 4,966,762 and a commercial sodium carbonate perhydrate containing silicate and magnesium stabilizer were coated with 2% and 10% borosilicate (about 50% sodium metaborate and 50% sodium silicate by weight). The samples were incorporated into non-phosphate Tide brand detergent to
30 provide 0.7% active oxygen (A.O.). The stability was determined after storage for 6 weeks in the Open Box Test. Results are reported in Table IV and compared with commercial Tide with Bleach detergent and with a sample of Tide brand detergent made up with sodium
35 perborate monohydrate.

The data show that while the coating improves the stability of the commercial sodium carbonate perhy-

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drate samples somewhat, that the stability of the SAPC with 2% coating is unexpectedly increased about fivefold.

EXAMPLE 6

5 The dissolution rate of coated peroxygen compounds was compared by measuring the change of active oxygen (A.O.) with time. Sufficient peroxygen compound was added to provide a final A.O. content of 0.2% by weight; the samples were stirred at 200 rpm.

10 Sodium perborate monohydrate (uncoated) which is known to dissolve very rapidly was substantially all in solution within 10 seconds, while uncoated sodium perborate tetrahydrate was only 50% dissolved by 120 seconds.

15 Samples of SAPC coated with 2% and 4% sodium borosilicate were both substantially dissolved (90%) within 40 seconds while samples of SAPC coated with 6%, 8% and 10% were all substantially dissolved (90%) within 60 seconds. A sample of SAPC coated with 2%
20 sodium silicate over an initial 2% sodium metaborate was only 80% dissolved after 120 seconds.

Coatings of more than 2% sodium metaborate alone agglomerated as they were too sticky to handle. This is contrary to the disclosures of Japanese Kokai 59-
25 193 999 which discloses that sodium metaborate should be employed in excess of sodium silicate when applied on sodium carbonate perhydrate (sodium percarbonate). Clearly, coating of SAPC with a combined sodium borate/sodium silicate (sodium metaborate) is far
30 superior than coating commercial sodium percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$).

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TABLE I

COMPARATIVE DECOMPOSITION RATE OF COATED
AND UNCOATED SODA ASH PEROXYGEN CARRIER

<u>Run</u>	<u>FMC Grade Soda Ash</u>	<u>Coating</u>		<u>Initial % AO</u>	<u>Quick Test cm/hr</u>
		<u>%</u>	<u>Compound</u>		
1	100	-	-	9.0	0.14
2	90	-	-	9.4	0.14
3	100	4	Sodium Silicate	9.0	0.07
4	100	10	Sodium Silicate	9.0	0.03
5	100	2	Sodium Silicate	9.0	0.09
6	100	2	Sodium Metaborate		
		2	Sodium Silicate*	9.0	0.06
7	100	2	Sodium Metaborate	9.0	0.27
8	100	2	Sodium Polyacrylate	9.0	0.09
9	100	2	Sodium Borosilicate	9.0	0.15
10	100	4	Sodium Borosilicate	9.0	0.06
11	100	10	Sodium Borosilicate	9.0	0.08
12	90	2	Sodium Borosilicate	9.4	0.12
13	90	4	Sodium Borosilicate	9.4	0.10
14	90	10	Sodium Borosilicate	9.4	0.12
15	100	2	Sodium Metaborate	9.0	0.09
16	90	2	Sodium Metaborate	9.4	0.12

*a second layer

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TABLE II

COMPARISON OF DECOMPOSITION OF COATED
AND UNCOATED PARTICLES
(NEAT AND FORMULATED INTO A DETERGENT)

Run	FMC Grade	% Coating	Neat SAPC		Detergent For- mulation
			% AO	Quick cm/hr	0.7% AO Quick Test cm/hr
1	100	2% NAMB	8.7	0.09	0.02
2	90	10% BORSIL	7.8	0.12	0.02
3	100	2% BORSIL	8.2	0.15	0.02
4	90	2% BORSIL	8.7	0.12	0.05
5	100	10% NASIL	7.0	0.07	0.00
6	90	10% NASIL	7.2	0.05	0.01
7	100	10% HMPHOS	7.9	0.15	0.03
8	100	2%NAMB/2%NASIL*	8.2	0.06	0.03
9	100	2% NASIL		0.09	0.05
10	100	2%NASIL/2%NAMB*	8.4	0.14	0.03
11	100	2% POLYAC		0.09	0.03
12	100	2%POLYAC/2%NASIL*	8.4	0.08	0.12
13	100	4% NASIL		0.07	0.03
14	100	4% NASIL	6.9	0.03	0.00
15	100	2%NASIL/2%NAMB*	8.1	0.08	0.04
16	90	2%NASIL/2%NAMB*	8.8	0.05	0.03
17	100	2%NAMB/2%NASIL*	8.4	0.04	0.04
18	90	2%NAMB/2%NASIL*	8.5	0.05	0.01
19	90	2%NASIL/5%NAMB*	8.0	0.06	0.01
20	100	2%NASIL/5%NAMB*	8.3	0.06	0.01
21	100	5%NAMB/2%NASIL*	7.6	0.04	0.02
22	90	5%NAMB/2%NASIL*	7.7	0.03	0.03

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TABLE II (cont'd.)

COMPARISON OF DECOMPOSITION OF SAPC ALONE
AND FORMULATED INTO A DETERGENT

<u>Run</u>	<u>FMC Grade</u>	<u>% Coating</u>	<u>SAPC</u>		<u>Detergent For- mulation 0.7% AO Hills Test cm/hr</u>
			<u>% AO</u>	<u>Hills cm/hr</u>	
23	100	UNCOATED	9.0	0.14	0.71
24	90	UNCOATED	9.4	0.14	0.64
25	Tide With Bleach		-	-	0.05

Key

NAMB	Sodium Metaborate
BORSIL	Sodium Borosilicate
NASIL	Silicate
HMPHOS	Sodium Hexametaphosphate
POLYAC	Polyacrylate

*indicates the
second layer

TABLE III
OPEN BOX STABILITY OF SAPC

<u>Run</u>	<u>FMC Grade Soda Ash</u>	<u>% AO</u>	<u>Coating % Comp.</u>	<u>Open Box Stability</u>					
				<u>% AO Retained After (in weeks)</u>					
				<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
1	100	8.8	2 NAMB	93	72	80	64	55	57
2	90	8.84	10 NASIL	100	72	62	67	58	56
3	90	7.93	10 NASIL	93	74	65	54	41	38
4	90	7.8	10 BOROSIL	100	96	94	84	77	70
5	100	8.2	2 BOROSIL	94	74	61	75	74	73
6	90	8.7	2 BOROSIL	94	83	61	60	53	53
7	Tide with Bleach			81	66	79	63	66	50
8	Uncoated 100 9.0			57	30	29	-	-	-
9	Uncoated 90 9.0			51	24	19	-	-	-

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TABLE IV

STABILITY OF SCP IN DETERGENT FORMULATION

<u>Sample</u>	<u>% Coat</u>	<u>% AO</u>	<u>6 weeks</u>
SAPC	2% Borosil	8.6	53
SAPC	10% Borosil	9.4	70
SAPC	None	9.0	9
PERC	None	13.6	19
PERC	2% Borosil	13.3	37
PERC	10% Borosil	11.8	57
Tide W/Bleach			50
Tide+SPBM		15.2	78

Borosil = sodium borosilicate

SPBM = sodium perborate monohydrate

SAPC = soda ash peroxygen carrier

PERC = commercial sodium carbonate perhydrate with
silicate/magnesium stabilizer

All test samples contain 0.7% A.O. in nonphosphorus Tide.

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Claims:

1. A process for preparing a storage-stable compound characterized by:

5 a) suspending substantially dry particles comprising sodium carbonate perhydrate containing 0.1% to 3% by weight of a diphosphonic acid or salt and between 1 and 5 moles of anhydrous sodium carbonate for each mole of available water contained therein sufficiently to substantially eliminate solid-solid
10 contact between particles,

b) contacting said dry particles with a plurality of fine drops of an aqueous solution consisting essentially of 10% to 90% by weight sodium silicate and 90% to 10% by weight sodium metaborate (sodium
15 borosilicate),

c) concomitantly evaporating water at a sufficient rate to avoid moistening or hydrating said dry particles thereby coating the particles with from 2% to 10% by weight of the sodium borosilicate, and

20 d) collecting the coated dry particles as a free-flowing peroxygen compound which is stable when incorporated into a solid detergent formulation.

2. The process of claim 1 wherein the aqueous solution consists essentially of 15% to 35% solids,
25 the solids consisting of 25% to 75% by weight sodium silicate and 75% to 25% by weight sodium metaborate.

3. The product made by the process of claim 1.

4. The product made by the process of claim 1 further characterized by having a bulk density of at
30 least 800 kg/m³.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US91/02308

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC(5): C01B 15/10 US CL.: 423/415P																							
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁷</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">Classification System</th> <th style="width: 80%;">Classification Symbols</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">US</td> <td style="padding: 5px;">252/186.27, 186.28, 186.29, 186.30, 186.31 423/415P</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	US	252/186.27, 186.28, 186.29, 186.30, 186.31 423/415P																	
Classification System	Classification Symbols																						
US	252/186.27, 186.28, 186.29, 186.30, 186.31 423/415P																						
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category ⁹</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, ,4759,956 26 July 1988 (AMER ET AL.) See abstract, column 5, lines 20-42.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4,321,301 23 March 1982 (BRICHARD ET AL.) See abstract, column 5, lines 25-50.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">P</td> <td style="padding: 5px;">US, A, 4,970,058 13 November 1990 (HILLS ET AL.) See abstract, claims.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">P</td> <td style="padding: 5px;">US, A, 4,966,762 30 October 1990 (PFEFFER ET AL.) See abstract, claims.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4,178,351 11 December 1979 (KLEBE ET AL.) See abstract, claims.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4,526,698 02 July 1985 (KURODA ET AL.) See abstract, claims.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4</td> </tr> </tbody> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	US, A, ,4759,956 26 July 1988 (AMER ET AL.) See abstract, column 5, lines 20-42.	1-4	Y	US, A, 4,321,301 23 March 1982 (BRICHARD ET AL.) See abstract, column 5, lines 25-50.	1-4	P	US, A, 4,970,058 13 November 1990 (HILLS ET AL.) See abstract, claims.	1-4	P	US, A, 4,966,762 30 October 1990 (PFEFFER ET AL.) See abstract, claims.	1-4	Y	US, A, 4,178,351 11 December 1979 (KLEBE ET AL.) See abstract, claims.	1-4	Y	US, A, 4,526,698 02 July 1985 (KURODA ET AL.) See abstract, claims.	1-4
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>																							
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center;">11 JULY 1991</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">26 JUL 1991</div> </td> </tr> <tr> <td style="padding: 5px;"> International Searching Authority <div style="text-align: center;">ISA/US</div> </td> <td style="padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;"> JOSEPH D. ANTHONY </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">11 JULY 1991</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">26 JUL 1991</div>	International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;"> JOSEPH D. ANTHONY </div>																	
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